Lecture 2

**Review of Basic Concepts**

Thermochemistry

**Enthalpy** – H  
heat content

H  Changes with all physical and chemical changes

$\Delta H^\circ$  Standard enthalpy (25°C, 1 atm)

(H=O for all elements in their standard forms – by definition)

<table>
<thead>
<tr>
<th><strong>Exothermic</strong></th>
<th><strong>Endothermic</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H &lt; 0$</td>
<td>$\Delta H &gt; 0$</td>
</tr>
<tr>
<td>Heat is released</td>
<td>Heat is absorbed</td>
</tr>
</tbody>
</table>

Because $\Delta H = (H \text{ products} - H \text{ reactants})$
Many special Enthalpy changes:

- fusion (melting) \((s \rightarrow l)\)
- vaporization \((l \rightarrow g)\)
- sublimation \((s \rightarrow g)\)
- ionization (loss of an \(e^-\) or electrons)
- electron affinities (capture of an \(e^-\) or electrons)

\(\Delta H: \) look at signs and rationalize

\[\text{e.g.,}\]

\[
\begin{align*}
\text{EXO} \quad \text{Cl}(g) + e^- & \rightarrow \text{Cl}^-(g) \quad \Delta H^\circ = -349 \text{ kJ/mol} \\
\text{EXO} \quad \text{O}(g) + e^- & \rightarrow \text{O}^-(g) \quad \Delta H^\circ = -142 \text{ kJ/mol} \\
\text{ENDO} \quad \text{O}^-(g) + e^- & \rightarrow \text{O}^{2-}(g) \quad \Delta H^\circ = 844 \text{ kJ/mol}
\end{align*}
\]
Bond Energies:

Simple case

\[
\text{HF(g)} \quad \rightleftharpoons \quad \text{H(g)} + \text{F(g)}
\]

\[\Delta H = 566 \text{ kJ/mol} \quad \text{ENDOTHERMIC}\]

The enthalpy of this process is the “H-F” Bond energy – the energy released when the H-F bond is formed.

Not so simple case…

\[
\text{H}_2\text{-N-NH}_2 \quad \rightleftharpoons \quad 2\text{N(g)} + 4\text{H(g)}
\]

\[\Delta H = 1724 \text{ kJ/mol}\]

↑

NOTE: This is not the bond energy for any of the bonds – It is a total enthalpy change.
Need to Estimate

If we know that:

\[
\text{NH}_3(g) \rightleftharpoons \text{N}(g) + 3\text{H}(g)
\]

\[\Delta H = 1172 \text{ kJ/mol}\]

Then \[E_{N-H} = \frac{1172}{3} = 391 \text{ kJ/mol}\]

If we assume this number is valid to use for Hydrazine, the formula of which is \(\text{H}_2\text{NNH}_2\) or \(\text{N}_2\text{H}_4\)

Then

\[E_{N-N} + 4E_{N-H} = 1724 \text{ kJ/mol}\]
\[E_{N-N} = 1724 - 4(391) = 160 \text{ kJ/mol}\]

... we have to live with these estimates
Thermochemical data can be tabulated by this method:

Table 1-1  Some Average Thermochemical Bond Energies at 25 °C (in kJ mol⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>C</th>
<th>Si</th>
<th>Ge</th>
<th>N</th>
<th>P</th>
<th>As</th>
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B. Multiple bond energies

C=C 598  C≡N 616  C=O 695  N≡N 418
C≡C 813  C≡N 866  C≡O 1073  N≡N 946

Use these values to calculate the energy that it would take to form a molecule.
Entropy and Free Energy

Two factors in chemical reactions:

1. Enthalpy, \( H \), (\( ^kJ/mol \))
   Energy (heat) dissipated

2. Entropy, \( S \), (\( ^kJ/Tmol \))
   State of organization
   “order versus disorder”
   which is a statistical probability

When \( \Delta H \) is more negative (exothermic) and \( \Delta S \) is more positive (more disordered) a reaction is more favored.

\[ \Delta G \text{ Free energy which is in } ^kJ/mol \]
Involves the relationship between \( \Delta H, \Delta S \)
\[ \Delta G = \Delta H - T\Delta S \text{ (T in degrees K) } \]
Example:

CH₂Cl₂ Heat of formation of Dichloromethane

C-H  H= 416 kJ/mol
C-Cl  H= 327 kJ/mol

2 x 416 + 2 x 327 = H_{formation} (CH₂Cl₂)
= 1308 kJ/mol

Using ΔG° as a Predictive Tool

ΔG° = \sum ΔG_f° (products) - ΔG_f° (reactants)

Of course

ΔG° = ΔH° - (298.15) ΔS°

(standard temperature)  T= 25°C or 298.15 K
The entropy change for a reaction is the difference between the absolute entropies of reactants and products.

\[ \Delta S^\circ = \sum S^\circ \text{ (products)} - S^\circ \text{ (reactants)} \]

**Q** When is \( S = 0 \)?

**A** At absolute zero for a perfectly crystalline solid

Now, what is the relationship between \( \Delta G \) and the Equilibrium Constant \( K \)?

\[ K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{aA + bB} \rightleftharpoons \text{cC + dD} \]

…recall
\[ \Delta G = -RT \ln K \]

↑

gas constant \( R = 8.314 \text{ J/Kmol} \)

at 25°C we have:

\[ \Delta G^\circ = -5.69 \log K_{298.15} \]

\( Q \) for \( \Delta G^\circ = 0 \) what is \( K \)?

\[ A = 1 \]

Note:
The more negative is \( \Delta G^\circ \), the more the reaction proceeds as written \( i.e. \ K \) is large so \( -5.69 \log K \) is getting larger and more negative. Conversely, the more positive is \( \Delta G^\circ \), the more the reaction will tend to the left ← rather then to the right → as written.
Q  How does a reaction become overall thermodynamically favored?

A  3 Ways.

First consider \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \)

1. \( \Delta H^\circ \) and \( \Delta S^\circ \) favor the reaction that is, \( \Delta H^\circ < 0 \), \( \Delta S^\circ > 0 \)

2. \( \Delta H^\circ \) favors the reaction, but \( \Delta S^\circ \) does not that is, \( \Delta H^\circ < 0 \), \( \Delta S^\circ < 0 \) but \( \Delta H^\circ \) is still more negative than \( T \Delta S^\circ \) is positive

3. \( \Delta H^\circ \) disfavors the reaction, but \( \Delta S^\circ \) favors it \( \Delta H^\circ > 0 \), \( \Delta S^\circ > 0 \) but \( T \Delta S^\circ \) is larger
Examples of all three types of situations:

1. formation of CO; SO₂  common case

\[ \frac{1}{2} \text{O}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons \text{CO}(\text{g}) \]
\[ \Delta G^\circ = -137.2 \text{ kJ/mol} \]
\[ \Delta H^\circ = -110.5 \text{ kJ/mol} \]
\[ T\Delta S^\circ = 26.7 \text{ kJ/mol} \]

In both cases:
- Enthalpy favors rxn
- Entropy favors rxn

\[ \text{S}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) \]
\[ \Delta G^\circ = -300.4 \text{ kJ/mol} \]
\[ \Delta H^\circ = -292.9 \text{ kJ/mol} \]
\[ T\Delta S^\circ = 7.5 \text{ kJ/mol} \]

2. synthesis of ammonia (NH₃)

\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \]
\[ \Delta G^\circ = -16.7 \text{ kJ/mol} \]
\[ \Delta H^\circ = -46.2 \text{ kJ/mol} \]
\[ T\Delta S^\circ = -29.5 \text{ kJ/mol} \]

- Enthalpy favors rxn
- Entropy disfavors rxn
3. rare

\[ \text{NaCl(s)} \rightleftharpoons \text{Na}^+(\text{ag}) + \text{Cl}^- (\text{ag}) \]

\[ \Delta G^\circ = -2.7 \]
\[ \Delta H^\circ = +1.9 \text{ (endothermic)} \]  
\[ T\Delta S^\circ = +4.6 \]

(less ordered in the dissolved form)

**Q** Does \( \Delta G^\circ \) value (sign) tell you whether a reaction will occur or not?

**A** NO. It tells you what is thermodynamically possible to attain at 25°C but does not tell you whether it will happen to an appreciable extent at 25°C simply upon mixing reactants.

**Q** What else needs to be considered?
A Kinetics or rate of the reaction. Activation energies for reactants to go to products can be very high, and the reaction will require a catalyst to occur. e.g. \( \text{NH}_3(g) \) synthesis

To occur, a reaction needs a \(-\Delta G^\circ\) and for the rate to be appreciable.

The study of \textbf{Kinetics} is the way we know the mechanism of a reaction \( \equiv \) how it occurs.

\textbf{Reaction conditions affect rate}
- Temperature, concentration, solvent, pressure, presence of a catalyst
One can write a rate law for any reaction

$$4 \text{HBr}(g) + \text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(g) + 2\text{Br}_2(g)$$

rate constant, $k$

$$\frac{d[\text{O}_2]}{dt} = -k \, [\text{HBr}] \, [\text{O}_2]$$

rate of disappearance of $\text{O}_2$ is related to the product of the concentration of the two reactants.

**Q** Did I make a mistake here?

Why isn’t the [HBr] concentration reflecting the molar ratio of the reaction?

$$4 \text{HBr}(g) + 1 \text{O}_2(g)$$?
No mistake. The rate law that best describes the speed of the reaction is the one based on a rate-limiting step. Obviously, in this reaction the rate limiting step is the reaction of one mole of O$_2$ with one mole of HBr.

$1 + 1 = 2$

2$^{nd}$ order reaction (sum of exponents on conc.)

What is a first order reaction?

One in which the rate law depends on the concentration of only one reactant.

(easy to envision in decomposition reactions)

$2N_2O_5(g) \rightleftharpoons 4 NO_2(g) + O_2 (g)$

$$\frac{d[N_2O_5]}{dt} = -k[N_2O_5]$$
Effect of temperature on Rates
Dependence of the rate constant, \( k \), on Temp., \( T \), in degrees Kelvin follows the Arrhenius Law

\[
K = A e^{-E_a/RT}
\]

- \( E_a \) is the activation energy
- \( A \) is called the “frequency factor”

- The higher the activation energy, the slower the reaction

- A plot of log \( K \) versus \( T \) allows for \( E_a \) to be determined